

REPORT		AD-A251 091		Form Approved OMB No. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 05-15-92		3. REPORT TYPE AND DATES COVERED Technical 06-01-91 to 05-31-92	
4. TITLE AND SUBTITLE The Absorption Spectrum of an Electron Solvated in Sodalite				5. FUNDING NUMBERS N00014-90-J-1159	
6. AUTHOR(S) K. Haug, V. Srdanov, G. Stucky, and H. Metiu					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of California Department of Chemistry Santa Barbara, CA 93106				8. PERFORMING ORGANIZATION REPORT NUMBER T3	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Chemistry Program 800 N. Quincy Street Alexandria, VA 22217				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Prepared for Publication in the Journal of Chemical Physics					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) <p>We use a simple model to study the color change taking place when sodium atoms are absorbed in the zeolite sodalite. The Hamiltonian is that of an electron moving in the electrostatic field created by the ions in the zeolite framework and by the alkali ion core. We examine the sensitivity of the absorption spectrum on the magnitude of framework charges, the orientation of the Na₄ cluster in the sodalite cells, the localization of the electron, the nature of the alkali impurity (Li, Na, K), and the laser polarization. Comparisons with the experiment help decide which framework charge models are consistent with the absorption spectrum.</p>					
14. SUBJECT TERMS				15. NUMBER OF PAGES 38	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	
				20. LIMITATION OF ABSTRACT UL	

OFFICE OF NAVAL RESEARCH

Contract N00014-90-J-1159
R&T Code 413n007

Technical Report No. 3

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by

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Prepared for Publication in

Journal of Chemical Physics

May 15, 1992

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THE ABSORPTION SPECTRUM OF AN ELECTRON SOLVATED IN SODALITE



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92-14086



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Abstract: We use a simple model to study the color change taking place when sodium atoms are absorbed in the zeolite sodalite. The Hamiltonian is that of an electron moving in the electrostatic field created by the ions in the zeolite framework and by the alkali ion core. We examine to what extent the absorption spectrum is sensitive to the magnitude of framework charges, the orientation of the Na_4 cluster in the sodalite cells, the localization of the electron, the nature of the alkali impurity (Li, Na, K), and the laser polarization. Comparing the calculated spectra with the experimental ones helps decide which framework charge models are consistent with the absorption spectrum.

I Introduction

Sodalite is a zeolite with the stoichiometric formula $(\text{Na}_3)^{3+} ([\text{AlSiO}_4]^-)_3$. It consists of a periodic arrangement of cages having the structure shown in Fig. 1. When sodalite is exposed to sodium vapor some of the cages trap a sodium atom to form the compound $(\text{Na}_4)^{4+}e^- ([\text{AlSiO}_4]^-)_3$. Here e^- denotes an electron that is no longer tightly bound to the absorbed sodium atom. In what follows we assume that the $(\text{Na}_4)^{4+}e^-$ cluster in this compound is a tetrahedron whose center coincides with that of an alumino-silicate cage. This assumption is based on the analogy with the compound hydroxysodalite, $(\text{Na}_4)^{4+}(\text{OH})^- [\text{AlSiO}_4]^-_3$, which has the same formula as the Na doped sodalite, with an OH^- group instead of an electron. X-ray diffraction studies^[1] of $(\text{Na}_4)^{4+}(\text{OH})^- [\text{AlSiO}_4]^-_3$ show that the oxygen atom of the $(\text{Na}_4)^{4+}\text{OH}^-$ cluster is in the middle of the sodalite cage, and the Na atoms are at the corners of a tetrahedron surrounding the OH^- group. ESR studies^[2] of $(\text{Na}_4)^{4+}e^- ([\text{AlSiO}_4]^-)_3$ show that e^- is located at the center of the $(\text{Na}_4)^{4+}$ cluster, just like OH^- in $(\text{Na}_4)^{4+}(\text{OH})^-$. These similarities prompt us to assume that the ions in $(\text{Na}_4)^{4+}e^-$ have the same tetrahedral structure as those of $(\text{Na}_4)^{4+}(\text{OH})^-$.

Doping sodalite with sodium causes a change of color, from transparent when sodium is absent, to light blue when the doping level is low, and to black when the sodalite is saturated^[3-5]. The process is reminiscent of the ionization of sodium dissolved in liquid ammonia, which turns blue because the solvated electron absorbs light.

Recently Srdanov *et al*^[6] have measured the absorption spectrum of Na doped sodalite in the low concentration limit. In this article we use a simple model for the electron - sodalite interactions to calculate this spectrum. The calculations have several goals. First, we want to understand the spectrum in terms of the electron dynamics in zeolite. Second, we wish to find which sets of framework charges are consistent with the observed spectrum. Third, we would like to know how sensitive the spectrum is to the structure of the Na₄ cluster. Fourth, we wish to know whether the polarization dependence of the absorption cross section contains enough information to make absorption experiments with single crystal zeolite worthwhile.

The properties of an electron "dissolved" in a cluster are of great current interest^[7]. The theoretical work on this subject^[7] is rather sophisticated, but uses several approximations to make the calculations feasible: the potentials are schematic, the adiabatic approximation is made and the nuclear degrees of freedom are sometimes treated classically. To find whether the results of such simulations are satisfactory it is necessary to compare them to experiments. Unfortunately, it seems to be difficult to achieve, in gas phase systems, the cluster density needed for the spectroscopic measurements. Furthermore, one is not quite certain that the clusters prepared experimentally have the same structure as the ones studied theoretically.

In view of these difficulties, the clusters encountered in zeolite systems have some advantages: it is not difficult to prepare samples with high cluster densities; moreover, since the clusters are likely to have a well defined orientation the laser polarization can be used to increase the dynamic

information. In gas phase experiments this information is degraded by orientational averaging. Finally X-ray diffraction measurements can determine the structure of the cluster and its orientation with respect to the framework.

The doped sodalite discussed here is a material of interest on its own. One can think of it as a collection of $(\text{Na}_4)^{4+}e^-$ clusters embedded in a quasi-rigid ionic "medium" provided by the aluminosilicate framework. The clusters occupy the sites of a periodic lattice and their concentration can be varied. At higher concentrations, the probability that two clusters occupy neighboring lattice sites is high. The electron wave functions of such neighbors overlap and this affects the optical and the electron transport properties of the material. The geometric and electrostatic parameters in these structures are very different from those encountered in metals or semiconductors. Moreover, they can be changed by modifying the shape and the size of the cages, and the charges on the framework. It is reasonable to hope that such materials will have unusual physical properties.

The article is organized as follows. In Section II we explain the theory used to calculate the absorption spectrum and in Section III we present the model used for the electron - zeolite interactions. Some computational details are discussed in Section IV and the results of the calculations in Section V.

II. THEORY

We consider a rigid sodalite framework containing an excess Na atom.
The Hamiltonian

$$H = p^2/(2m) + V(r; R, Q) \quad (\text{II.1})$$

contains the kinetic energy of the electron plus its interaction energy with the framework atoms. The electron position and momentum are r and p , respectively. The positions of the Na ions and of the framework atoms are symbolically indicated by R and their charges by Q .

Because the electron excitation gap (about 2 eV) is much larger than $k_B T$ (0.026 eV at 300K), the electron is initially in the ground state $\langle x, y, z | g \rangle \equiv g(x, y, z)$. We calculate this from

$$\langle x, y, z | g \rangle = \lim_{\beta \rightarrow \infty} \langle x, y, z | \exp [-\beta H] | \Psi \rangle \quad (\text{II.2})$$

where β is a real number with units of energy⁻¹. For $\langle x, y, z | \Psi \rangle \equiv \Psi(x, y, z)$ one can use any normalizable function that has a nonzero projection on the ground state. The numerical procedure used to evaluate $|g\rangle$ from (II.2) has been described by Hellsing, Nitzan and Metiu^[8].

To calculate the absorption cross section $\sigma(\omega)$ we use a slight modification of Heller's formula^[9]

$$\sigma(\omega) = \omega \operatorname{Re} \int_0^\infty dt \exp(i\omega t) C(t). \quad (\text{II.3})$$

The overlap integral $C(t)$ is:

$$C(t) = \exp(iE_g t/\hbar) \langle \Phi(0) | \Phi(t) \rangle. \quad (\text{II.4})$$

with

$$|\Phi, 0\rangle = \epsilon \cdot \mathbf{r} |g\rangle \quad (\text{II.5})$$

and

$$|\Phi, t\rangle = \exp(-iH t/\hbar) |\Phi, 0\rangle. \quad (\text{II.6})$$

E_g is the ground state energy of the electron and ϵ is the polarization vector of the laser. The propagator in (II.6) is evaluated with the Fleck, Morris and Feit^[10] method. We call $|\Phi, 0\rangle$ the promoted state.

Heller has pointed out^[9] the connection between the resolution of the absorption spectrum and the length of time in which the promoted state explores the potential energy surface. This was used by Engel, Schinke, Henning and Metiu^[11] to obtain dynamic information by generating a sequence of low resolution spectra:

$$\sigma(\omega; \tau) \sim \omega \operatorname{Re} \int_0^\infty dt f_\tau(t) \exp(i\omega t) C(t). \quad (\text{II.7})$$

The "window" function

$$f_{\tau}(t) = \exp[-(t/\tau)^2]. \quad (\text{II.8})$$

cuts off the time evolution of the overlap integral at times longer than τ . In the frequency domain, this broadens the spectrum and generates a version having the resolution $\Delta\omega=2/\tau$. Thus, a spectrum taken with the resolution $\Delta\omega$ contains information about the motion of the promoted state for a time $\tau = 2/\Delta\omega$.

The measurements^[6] are made on a sodalite powder. To compare our calculations with the results of the experiment we evaluate

$$\sigma(\omega; \tau) = (1/N) \sum_{n=1}^N \sigma_n(\omega; \tau). \quad (\text{II.9})$$

The cross sections σ_n corresponds to a particular polarization direction with respect to the zeolite framework. The sum is over a representative sample of directions and Na_3 orientations (see Section V.6).

III. THE MODEL FOR $V(\mathbf{r}; \mathbf{R}, Q)$

The electron interaction with the framework and the alkali ion is described by two body spherically symmetric, energy independent, local pseudopotentials^[12].

The energy of the interaction between the electron and the framework ions is

$$V(\mathbf{r}; [\mathbf{R}, Q]) = \sum_i -e^2 Q_i \exp[-(|\mathbf{r}-\mathbf{R}_i|/\Lambda)^2] / \min[|\mathbf{r}-\mathbf{R}_i|, R_i^c]. \quad (\text{III.1})$$

The atoms forming the zeolite frame are treated as point charges Q_i located at the positions R_i . The electron charge is denoted e and R_i^c is a cutoff distance which truncates the coulomb potential. This form, suggested by Shaw^[12b], has been used for modeling the dynamics and absorption spectrum of an excess electron in a variety of atomic clusters^[7]. The cut off is used to eliminate the effect of remote charges. The smooth exponential cut off, $\exp[-(|r-R_i|/\lambda)^n]$, is preferable when the numerical method uses Fourier transforms. We use $\lambda = 15.0 - 25.0 \text{ \AA}$ and $n=4$. Including the zeolite atoms located between 40 and 53 \AA from the grid center does not affect the spectrum. To calculate the energy of the electron-framework interaction we use about 16,000 zeolite atoms; we include all atoms within 40 \AA from the grid center.

The charges Q_i and the cutoff distances R_i^c used in Eq.(III.1) are given in Table I. The values of R_i^c are chosen such that the two body interaction between the electron and atom "i" approximates the ionization potential of the corresponding ion (or atom) with charge Q_i . For example, if we deal with the ion A^{2+} the cut-off distance is chosen so that the interaction between e^- and A^{2+} gives a reasonable value for the ionization potential of A^+ . The values chosen for Na^+ are discussed in Section V.1.

Approximation the interaction potentials by electrostatic point charge interactions or by point dipoles goes back to the crystal field theory (CFT) of Bethe in the 1920's^[13]. The magnitude of the charges is still unsettled. Assuming that the ionic charges are those suggested by the valence of the atoms (e.g. 3 for Al, -2 for O) fails dramatically for some cases (as it would for ours - see Section V).

Using his definition of electronegativity, Pauling^[14] concluded that zeolites are ionic crystals with 50% ionicity. Density functional theory proposes^[15] a different definition for electronegativity which leads to different charges. Since there is no widely accepted set of charges we calculate the absorption spectrum for several charge distributions, denoted by a, b, c, d, and e in Table I. The comparison of the computed spectra with the measured ones helps establish which proposals are compatible with the observed optical properties.

The a-model uses the smallest charge^[16]. These charges were arrived at by regarding the sodalite framework as a neutral SiO_2 framework in which some O atoms were replaced with Al. The fractional charges used by the model are caused by the imbalance generated by this substitution. The alkali counterions take on a +1 charge to maintain charge balance with the fractional negative charge on the oxygens. The b-model is an interpolation between the a-model and the c-model. The c-model is based on the work of Leherste, *et. al.*^[17] who use Mulliken *ab initio* STO-3G atomic net charges to suggest for the ferrierite zeolite about a +1.5 charge on the Si atoms and a -0.7 charge on oxygen. The d-model is from Van Genechten, *et. al.*^[18] who use electronegativity equalization methods to place a +1.9 charge on the Si atoms in sodalite and a -0.95 charge on oxygen. The e-model is an interpolation between the d-model and a model suggested by Skorczyk^[19] who places a +3.03 charge on the Si atoms, +2.45 on the Al, and -1.62 on the oxygen.

IV. COMPUTATIONAL DETAILS

The Feit, Morris, and Fleck^[10] split operator method used to evaluate how

$\exp(-iHt/\hbar)$ and $\exp(-\beta H)$ modify a given wave function use a time step of 0.01fs and a β step size of 0.05 eV^{-1} . The three dimensional spatial grid has 48 points with a spacing of 0.546 \AA in each direction. We tested the convergence of the numerical method by performing calculations with smaller and smaller time, β , and spatial steps until the spectrum did not change. A grid with 64 points and a step of 0.4095 \AA , which covers 3 unit cells in each 4-fold symmetry direction, and also a grid covering 4 unit cells in each 4-fold symmetry direction shifted the ground state energy of the electron by 0.02eV (about 0.5%) and the promoted state energy by 0.01eV (about 0.4%). We typically propagate the system for a time length of 30 to 120 fs. For this period the converged results conserve energy to within about 0.2%.

V. RESULTS

V.1 The spectrum of the isolated Na atom

The absorption spectrum of the isolated Na atom is obtained by suppressing in the Hamiltonian all but the Na ion - electron interaction. We have computed it to test whether using a truncated coulomb potential is reasonable and to compare it with the spectrum of the Na atom absorbed in sodalite.

In Fig. 2 we show the absorption spectrum of the sodium atom with the cut off parameter $R_c^e = 1.725 \text{ \AA}$. This value gives an ionization potential of 5.139 eV . The time constant τ of the window function is 40 fs. This gives a line width on the order of \hbar/τ .

The calculated ionization potential, oscillator strengths and peak frequencies are compared to the measured^[20] ones in Table II. The oscillator

strengths and frequencies of the first two peaks in the calculated spectrum agree with the measured ones quite well.

Since the pseudopotential is spherically symmetric the dipole selection rules allow transitions from the s ground state to the np_z states (the z axis was taken parallel to the laser polarization). The transition intensity is highest for $1s \rightarrow 2p_z$ and decreases with n .

V.2 The dependence of the absorption spectrum on the framework charges.

It is useful to think of the sodium doped sodalite $(Na_4)^{4+}e^-([AlSiO_4]^-)_3$ as an electron in an ionic system consisting of a tetrahedral sodium cluster $(Na_4)^{4+}$ imbedded in the alumino - silicate framework of the zeolite. To understand how the framework affects the electron we examine first the isolated $(Na_4)^{4+}e^-$ system. The dimensions of the $(Na_4)^{4+}$ tetrahedron are the same as inside the zeolite. This spectrum serves as a reference used to examine the influence of the zeolite framework. The absorption spectrum (Fig. 3) of $e-(Na_4)^{4+}$, was calculated for the laser polarization shown in Fig. 4. The tetrahedral field of the ions breaks the spherical symmetry and splits the peaks appearing in the spectrum of the isolated Na atom (Fig. 2). The peak positions are shifted and the ionization potential is 18.82 eV. Considering the enormous difference in the ionic charge, the similarity between the spectra of Na and that of $e-(Na_4)^{4+}$ is rather surprising. This similarity is partly due to the small size of the tetrahedron which makes the potential energy felt by the electron almost spherically symmetric.

Next we study how the framework charges affect the properties of the electron when the $(Na_4)^{4+}e^-$ cluster is located inside the sodalite. The spatial distribution of the electron in the ground state $g(x,y,z)$ is characterized by

$$P(r_1, r_2) = \int_{r_1}^{r_2} r^2 dr \sin(\theta) d\theta d\phi |g(r, \theta, \phi)|^2. \quad (V.1)$$

The values of r_1 and r_2 are chosen so that we obtain the probability of finding the electron in the $(Na_4)^{4+}$ tetrahedron region, on the nearest alumino - silicate shell or in the region outside the unit cell in which the tetrahedron is located. The results of these calculations are given in Table III.

For the models a through d the electron tends to remain localized inside the tetrahedron (see Table III). The only exception is model e for which the probability that the electron is located outside the unit cell containing the tetrahedron is high. ESR experiments^[2] on sodalite, suggest that the excess electron is localized around the $(Na_4)^{4+}$ tetrahedron. Moreover, the absorption spectrum for the model e is rather different from that observed experimentally. For these reasons we abandon model e and concentrate in what follows on the models (a-d).

In Fig. 5 we show the spectra of the doped sodalite, for the charge distributions a,b,c,d of Table I, and the laser polarization shown in Fig. 3. The magnitude of the charges is progressively higher as we go from model a to model d (Table I). The spectrum begins shifting dramatically only when the ionic character of the zeolite atoms is close to 50% (model-d of Table I). Only in the d-model the forces due to the framework charges are large enough to compete with those exerted by the $(Na_4)^{4+}$ tetrahedron.

V.3 The absorption spectrum and electron dynamics time scales

We examine here the connection^[11] between the absorption spectrum and the time scales of electron dynamics.

In Fig.6 a,b,c we show the spectra for the d-model (see Table I) of the doped sodalite for three different resolution times, $\tau = 5, 20$, and 40 fs. For $\tau = 5$ fs, the energy resolution is on the order of 1 eV and for 40 fs it is on the order of 0.1 eV. The presence of two bands in the spectrum is discerned even if the electron samples the potential for 5 fs. Sampling for 20 fs is enough to resolve the presence of three peaks, and a 40 fs sampling resolves all the structure. Further sampling will only narrow the lines obtained at 40 fs. On this time scale the nuclear motion does not have time to affect the spectrum. If the motion of the framework is included it will contribute low frequency phonon side bands which have little information regarding the electron dynamics.

To get a better feeling for the kind of motion that generates the spectrum we examine the evolution of the mean radial electron position $\langle r \rangle_t$ for the time dependent promoted state. In the $e^-(Na_4)^{4+}$ cluster $\langle r \rangle_t$ undergoes localized oscillations with a maximum amplitude of about 0.4 Å. When the cluster is imbedded in the the d-model sodalite the electron performs more extensive excursions under the influence of the framework charges with a maximum amplitude of about 1.7 Å.

In Fig. 7 we plot the probability $P(r_1, r_2; t)$ that the electron in the promoted state is located between r_1 and r_2 (see Eq. (V.1)), for the d-model. Here r denotes the radial distance measured from the center of the unit cell (which coincides with the center of the Na^{4+} tetrahedron) Initially the promoted state, like the electron ground state, is localized around the tetrahedron; 83% of the electron

density is within 3.4 Å of the center (each Na^+ is located at 2.401 Å from the center). There is a 16% probability that the electron is in the region of the closest zeolite shell (between 3.4 and 5.4 Å). Only 1% of the electron density extends into the surrounding cages.

In the first five fs 50 to 80% the electron density moves into the surrounding cages at the expense of the population around the tetrahedron. This suggests that the excited states that carry oscillator strength are delocalized and extend into the neighboring zeolite cells. For the isolated Na atom or the bare $(\text{Na}_4)^{4+}$ e- cluster the probability density of the promoted state changes very little in time. Another way to interpret this calculation is that if excited with a δ -function pulse the electron will move out of the Na^{4+} trap in five femtosecond. This suggests that if the trap concentration is low the material will photoconduct.

V.5. The dependence of the spectrum on the dimensions of the Na_4 cluster.

So far we have assumed that the $(\text{Na}_4)^{4+}$ cluster in the sodalite cage has the same dimension and orientation as the $(\text{Na}_4)^{4+}$ cluster in hydroxysodalite. We have done this out of necessity, since no X-ray studies of the doped sodalite are available. The absorption spectrum is very sensitive to the distance d_1 between the Na ion and the center of the cell (which is the same as the center of the tetrahedron) (Fig.8). The ground state energy also changes from -4.594eV for $d_1=2.601\text{Å}$ to -6.1388eV for $d_1=2.301\text{Å}$. This sensitivity to the size of the tetrahedron makes the X-ray study of sodium doped sodalite essential for a detailed understanding of the absorption spectrum. It also suggests that materials differing through the composition of the tetrahedron are likely to have

substantially different properties.

V.6. The dependence of the spectrum on the orientation of the Na_3 clusters.

The spectrum may also be influenced by the orientation, the size and the positions of the $(\text{Na}_3)^{3+}$ clusters located in the cells surrounding the one occupied by the $(\text{Na}_4)^{4+}$ cluster. Since the $(\text{Na}_3)^{3+}$ clusters do not show up in diffraction studies, we may assume that their orientation is random. The observed spectrum is then the average over all these orientations. As shown by Fig. 9 the spectrum changes significantly with the orientation of the $(\text{Na}_3)^{3+}$ clusters. Since the ground state of the electron is very well localized around the Na_4 tetrahedron, the dependence of the spectrum on the orientation of the Na_3 clusters in the adjacent cells is another indication that the excited states are delocalized.

The spectrum is also sensitive to the size of the $(\text{Na}_3)^{3+}$ clusters (Fig. 10) from the cells surrounding the one in which the tetrahedron is located. The $(\text{Na}_3)^{3+}$ clusters are assumed to be an equilateral triangle characterized by a distance d_2 from a Na atom to the cell center. As the surrounding $(\text{Na}_3)^{3+}$ groups become smaller, the electron ground state is more extended. If $d_2 = 1.38\text{\AA}$, for the d-model, the probability of finding the electron within 3.4\AA from the tetrahedron's center is only 3%; the probability of finding the electron around the $(\text{Na}_3)^{3+}$ clusters exceeds 90%. This is inconsistent with the esr data which suggest that the electron is localized within the Na_4 cluster.

V.7. Polarization effects

The existing experiments have been performed with powders but

experiments with doped single crystals are possible. In this case one controls the direction of the electric field with respect to the frame of the zeolite. If the sodium clusters inside the zeolite are ordered varying the laser polarization may be informative. For this reason we examine the spectrum for the model-c for 2 different polarizations (Fig. 11). The energy levels in the two spectra must be identical and the only difference is in the intensities. The appearance of a new peak does not mean that the system has a new eigenstate but that the change in polarization has changed the oscillator strength of the state.

V.8. Alkali substitution effects

It is not difficult to dope sodalite with other alkali atoms. In anticipation of such experiments we have examined the absorption spectrum obtained by adding Li or K atoms (Fig. 12). From top to bottom, the three panels in Fig. 12 are spectra of the K, Na and Li doped sodalite, respectively. In our model these atoms differ through the cutoff distance R^c_i in Eq.(III.1) (see Table IV). The most notable trend is a blue shift in going from K to Na to Li impurity.

Acknowledgements: The authors are grateful to the Science and Technology Center QUEST and to the Office of the Naval Research, for supporting this work.

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FIGURE CAPTIONS

Fig. 1: One cage in the sodalite matrix. The Al and Si atoms are at vertices and they alternate. There is one O atom on each line. The Na atoms sit inside of the cages. The sodalite is a space-filling periodic collection of such cages.

Fig. 2: The absorption spectrum of the sodium atom for the potential given by Eq.(III.1) using $\tau = 40\text{fs}$ in Eq.(II.8). The low intensity absorption cross section $\sigma(\omega)$, in arbitrary units, is plotted versus energy in units of eV. The intensities of the first two peaks, which go off the scale, are 911.8 and 53.9 in the arbitrary units used here.

Fig. 3: The absorption spectrum of the $(\text{Na}_4)^{+4}\text{e}^-$. The same parameters as for Fig. 2. The intensities of the first two peaks, which go off the scale, are 1876.5 and 928.3 in the arbitrary units used here.

Fig. 4: The orientation of the $(\text{Na}_4)^{+4}$ tetrahedron in the coordinate system used. The polarization of the laser electric field is specified with respect to the same coordinate system.

Fig. 5: The absorption spectrum $\sigma(\omega)$ of the a,b,c,and d-models for framework charges (Table I). We used $\tau = 30\text{ fs}$ in Eq.(II.8).

Fig. 6: A sequence of absorption spectra with the time resolutions a) $\tau=5\text{ fs}$, b) $\tau=20\text{ fs}$ and c) $\tau=40\text{ fs}$.

Fig. 7: The time evolution of the probability that the electron in the promoted state is located at various distances from the center of the cell (see Eq.V.1): (a) $0 \leq r \leq 3.4\text{ \AA}$ (the solid line); (b) $3.4\text{ \AA} \leq r \leq 5.4\text{ \AA}$ (the short dashed line); and (c) $5.4\text{ \AA} \leq r \leq 12.0\text{ \AA}$ (the long dashed line).

Fig. 8: The absorption spectra for the d model for various tetrahedron sizes d_1 . (a) $d_1=2.601\text{\AA}$; (b) $d_1=2.501\text{\AA}$; (c) $d_1 = 2.401\text{\AA}$; (d) $d_1=2.301\text{\AA}$.

Fig. 9: The spectra of the d-model sodalite for two different orientations of the $(\text{Na}_3)^{3+}$ groups in the sodalite.

Fig. 10: Spectra of the d-model sodalite for three sizes of the $(\text{Na}_3)^{3+}$ clusters, characterized by the distance d_2 from the ions to the center of the cluster (which is an equilateral triangle). (a) $d_2=2.501\text{\AA}$; (b) $d_2=2.401\text{\AA}$; (c) $d_2=2.301\text{\AA}$.

Fig. 11: Spectra of the d-model sodalite laser polarizations. (a) The electric field is in the z-direction (see Fig. 4). (b) The electric field is in the x-direction.

Fig. 12: The spectra of sodalite doped with (a) K , (b) Na , or (c) Li. We assume the same structure for the tetrahedron. The only difference is the electron alkali interaction.

TABLE I:

The charges on the zeolite framework. Q_i is the charge and R_i^c is the cutoff distance used for species i in the interaction potential in Eq.(III.1).

Model	a	b	c	d	e
Q_{Na}	+1.0	+1.0	+1.0	+1.0	+1.0
Q_{Si}	0.0	+1.0	+1.5	+1.9	+2.5
Q_{Al}	0.0	+0.8	+0.85	+0.9	+1.7
Q_O	-0.25	-0.7	-0.8375	-0.95	-1.3
R_{Na}^c	1.725	1.725	1.725	1.725	1.725
R_{Si}^c	—	0.77	0.68	0.60	0.50
R_{Al}^c	—	1.66	1.55	1.50	1.00
R_O^c	0.20	0.20	0.20	0.20	0.20

TABLE II:

The ionization potential (IP), the oscillator strengths (f_i) and the peak frequencies (ω_i) for our Na atom model, compared to measured values.

	Na Model	Na Measured ^a
IP (eV)	5.139	5.139
f_1	0.975	0.95-1.0
f_2	0.017	0.014
f_3	0.005	0.002
ω_1 (eV)	2.22	2.10
ω_2 (eV)	3.78	3.75
ω_3 (eV)	4.59	4.34

(a) Measured values of the oscillator strengths are taken from Ref.20 [H.G. Kuhn -Atomic Spectra, Second Edition, Longmans, London, 1969, p173] while the peak frequencies are taken from Ref. 21 [A.R. Stiganov and N.S. Sventitskii, Tables of Spectral Lines of Neutral and Ionized Atoms, Plenum, New York , 1968]

TABLE III:

Probability distributions of the ground state [$P(r_1, r_2)$ from Eq.(V.1)] for various framework charges (models a,b,c,d and e in Table I). Distances are given in Angstroms.

Model	a	b	c	d	e
P(0.0, 3.4)	0.97	0.97	0.97	0.96	4.(-3)
P(3.4, 5.4)	2.7(-2)	2.6(-2)	2.8(-2)	3.7(-2)	0.12
P(5.4, 12.0)	6.(-4)	5.(-4)	7.(-4)	2.(-3)	0.87

TABLE IV:

The ionization potentials (IP) and the cutoff distances R_i^c used in Eq.(III.1) for Li, Na and K impurities.

Element	Li	Na	K
R_i^c (Å)	1.61	1.725	2.21
Calculated IP (eV)	5.39	5.14	4.34
Measured IP (eV)	5.39	5.14	4.34

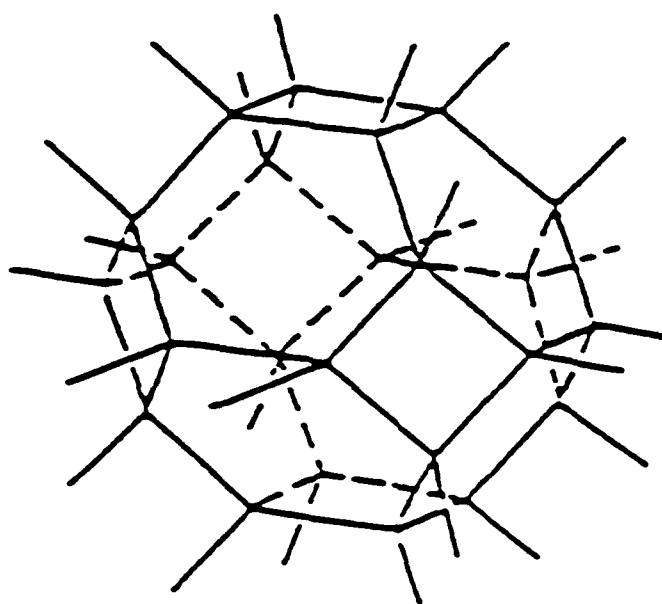


Fig 1

Fig. =

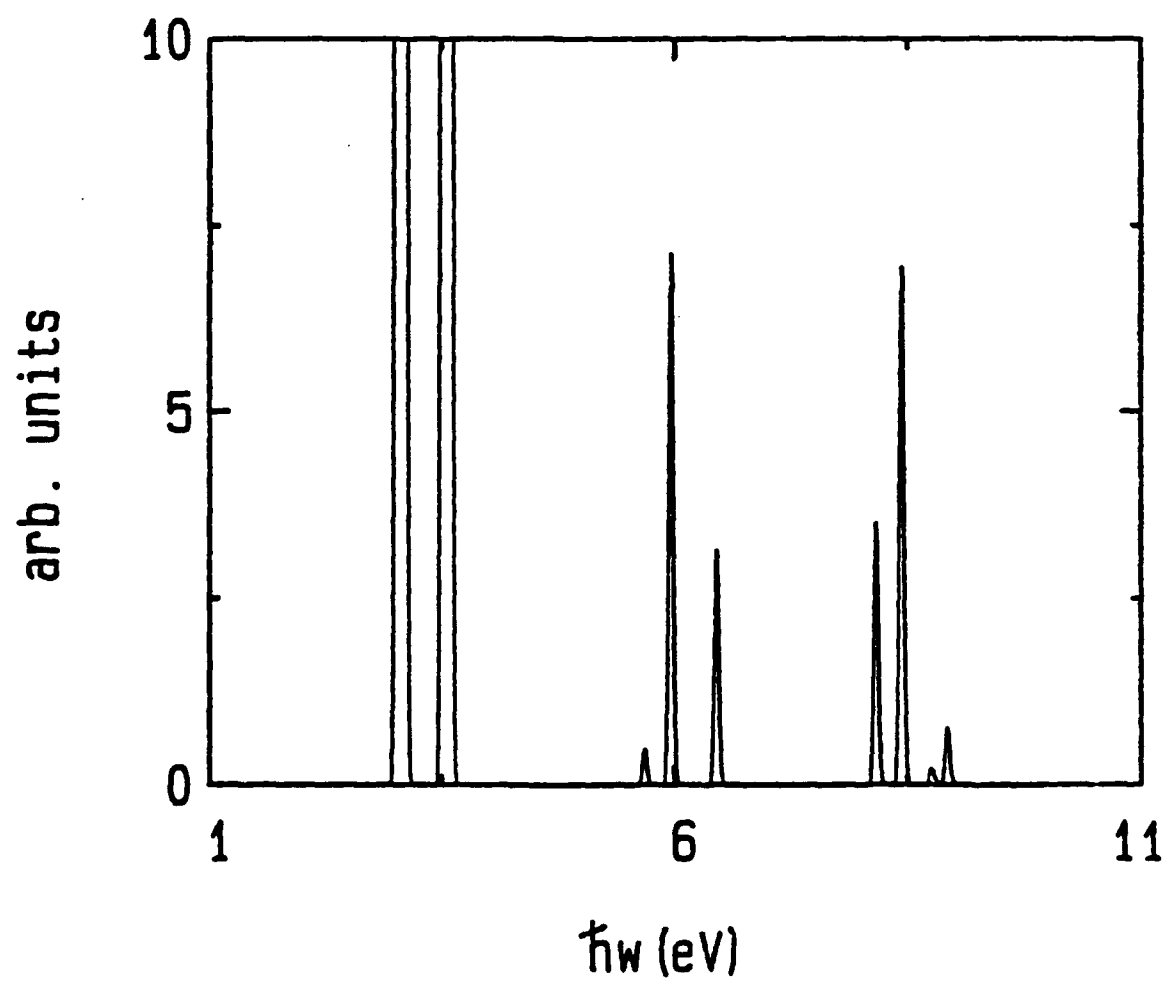


Fig. 4

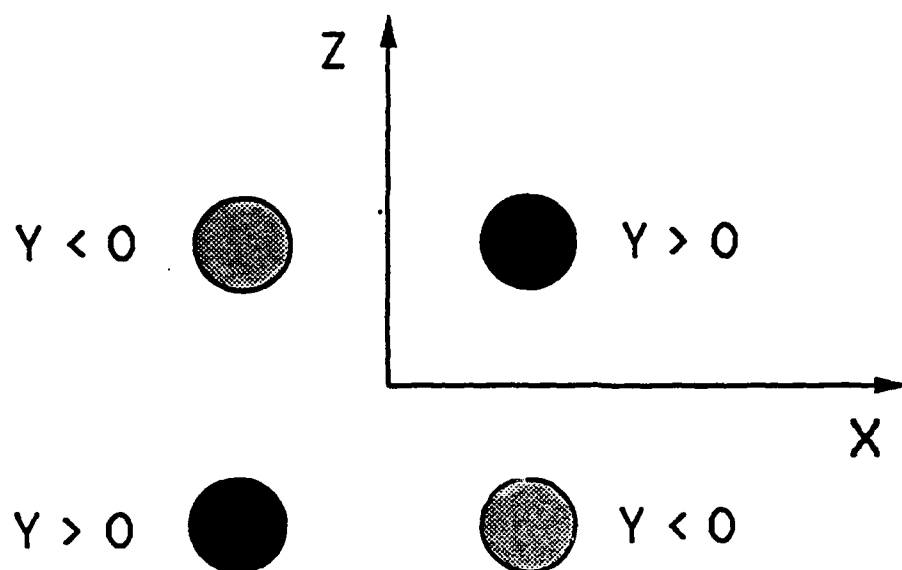


Fig. 5

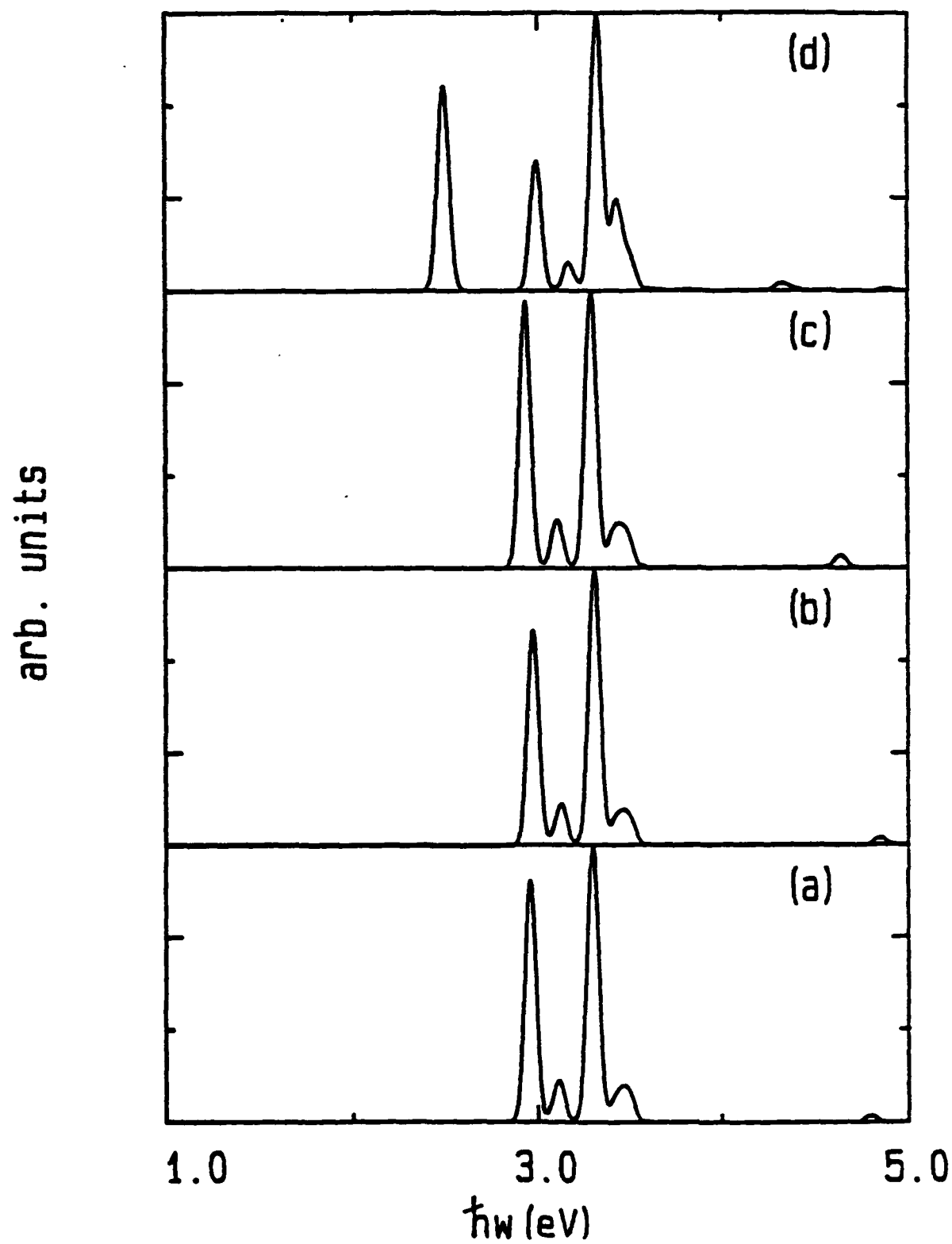


Fig 6

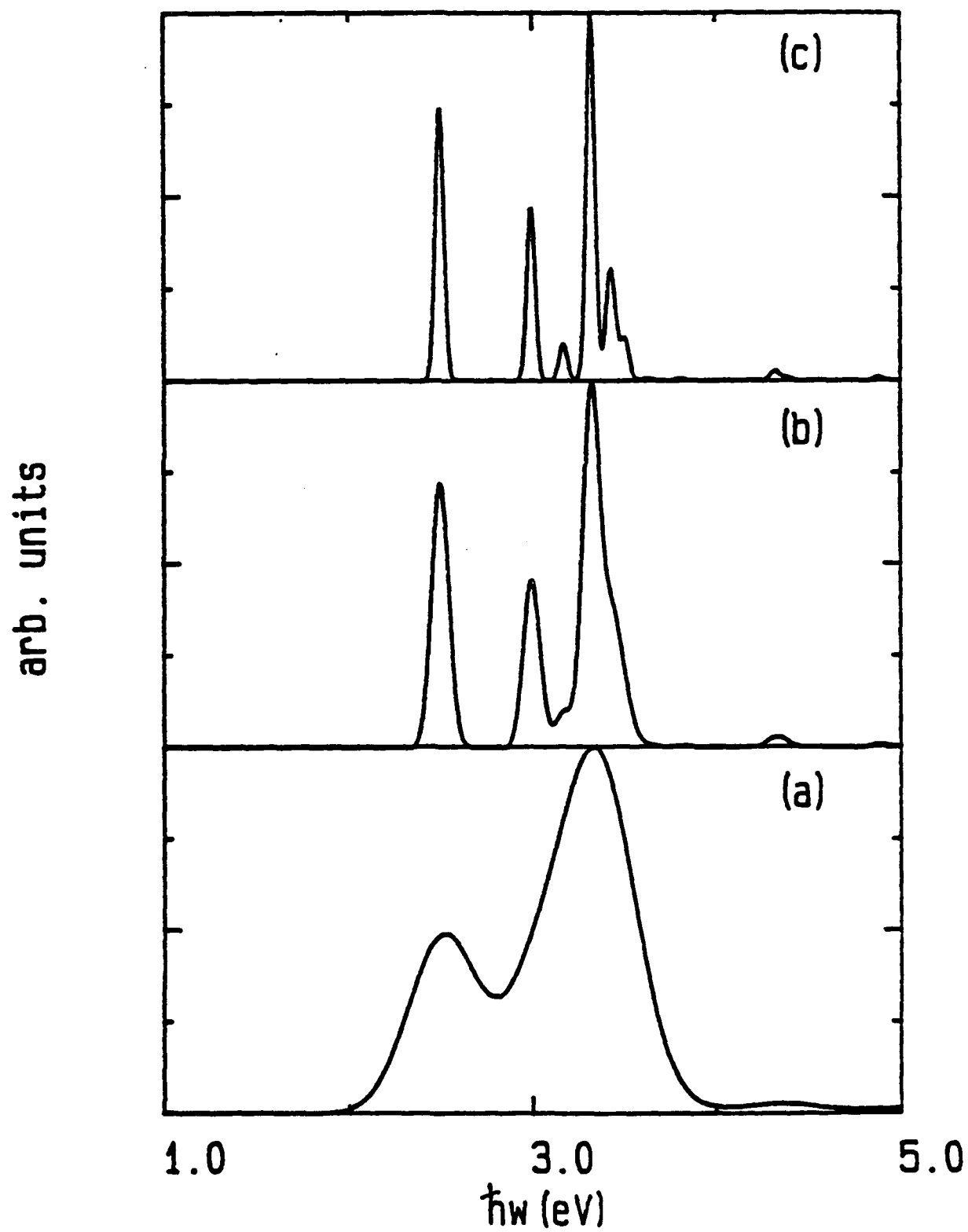


Fig. 1

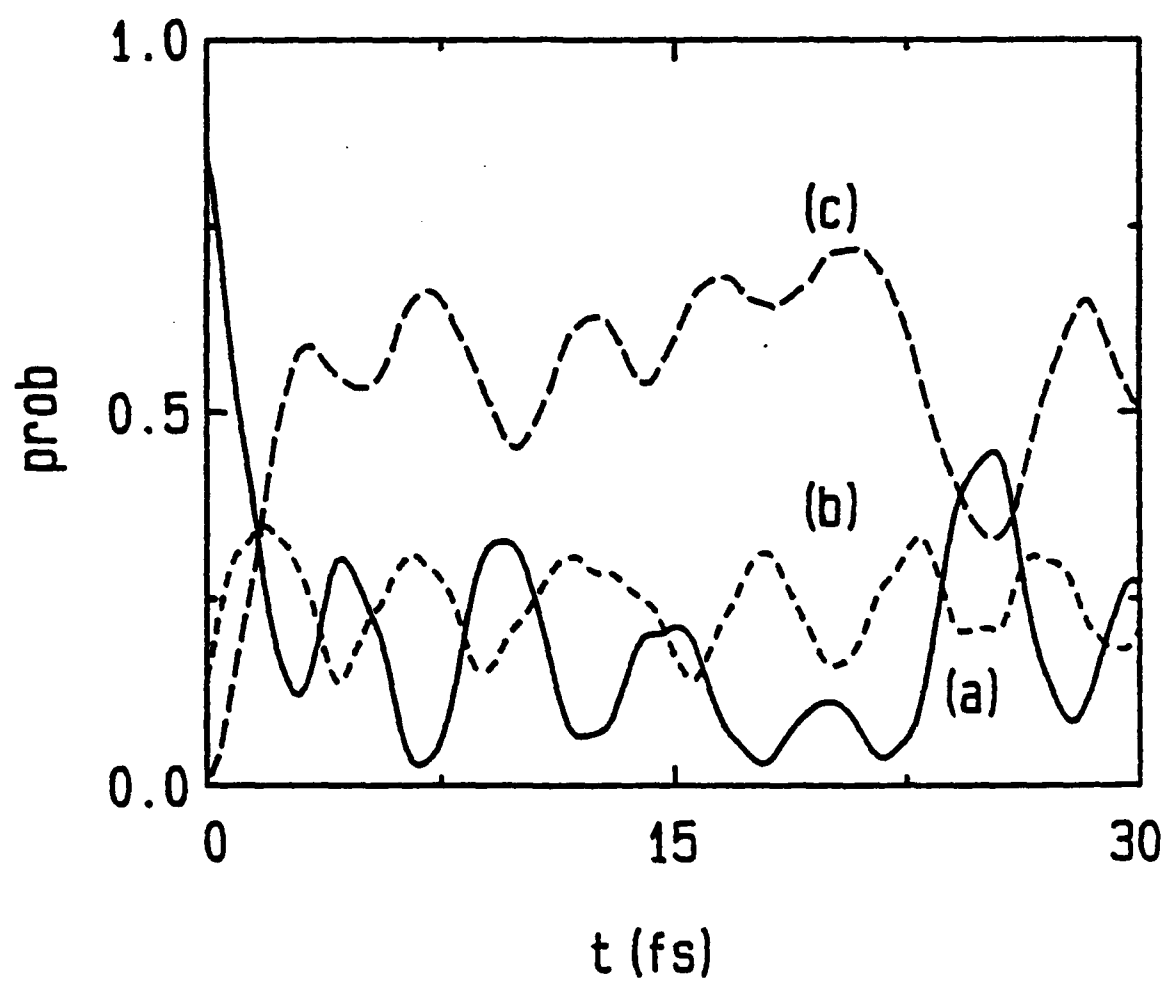


Fig. 8

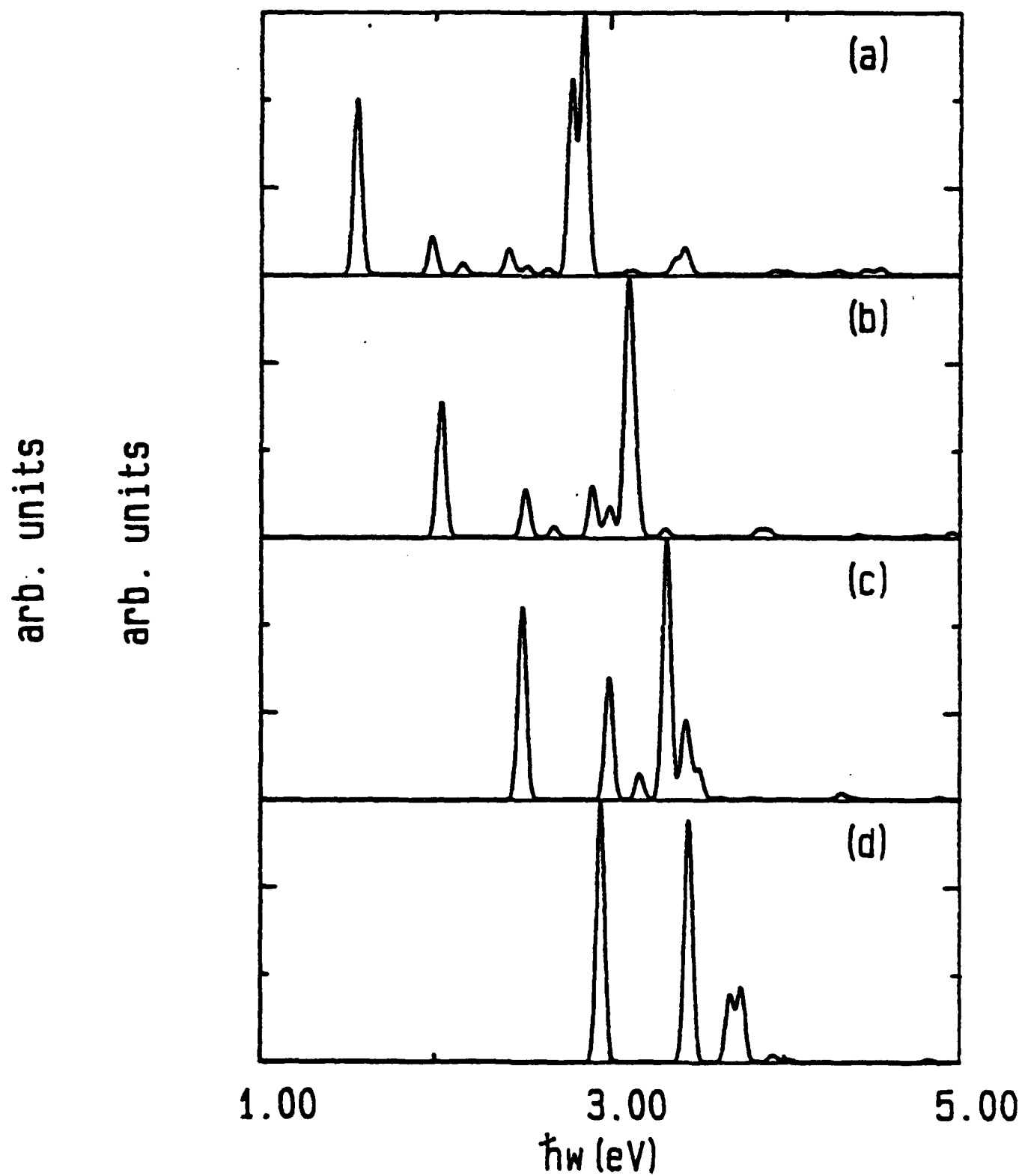


Fig 9

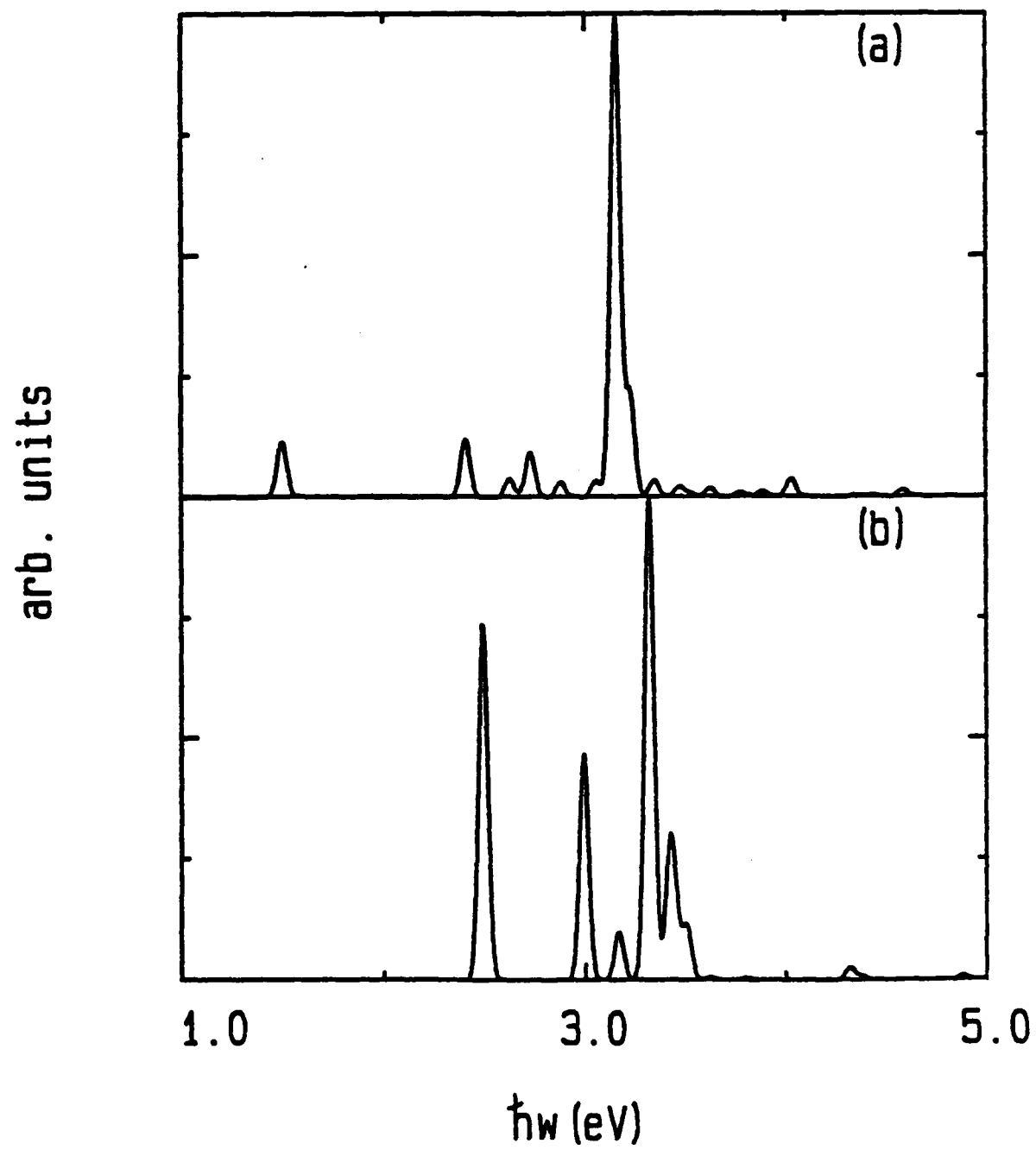


Fig 10

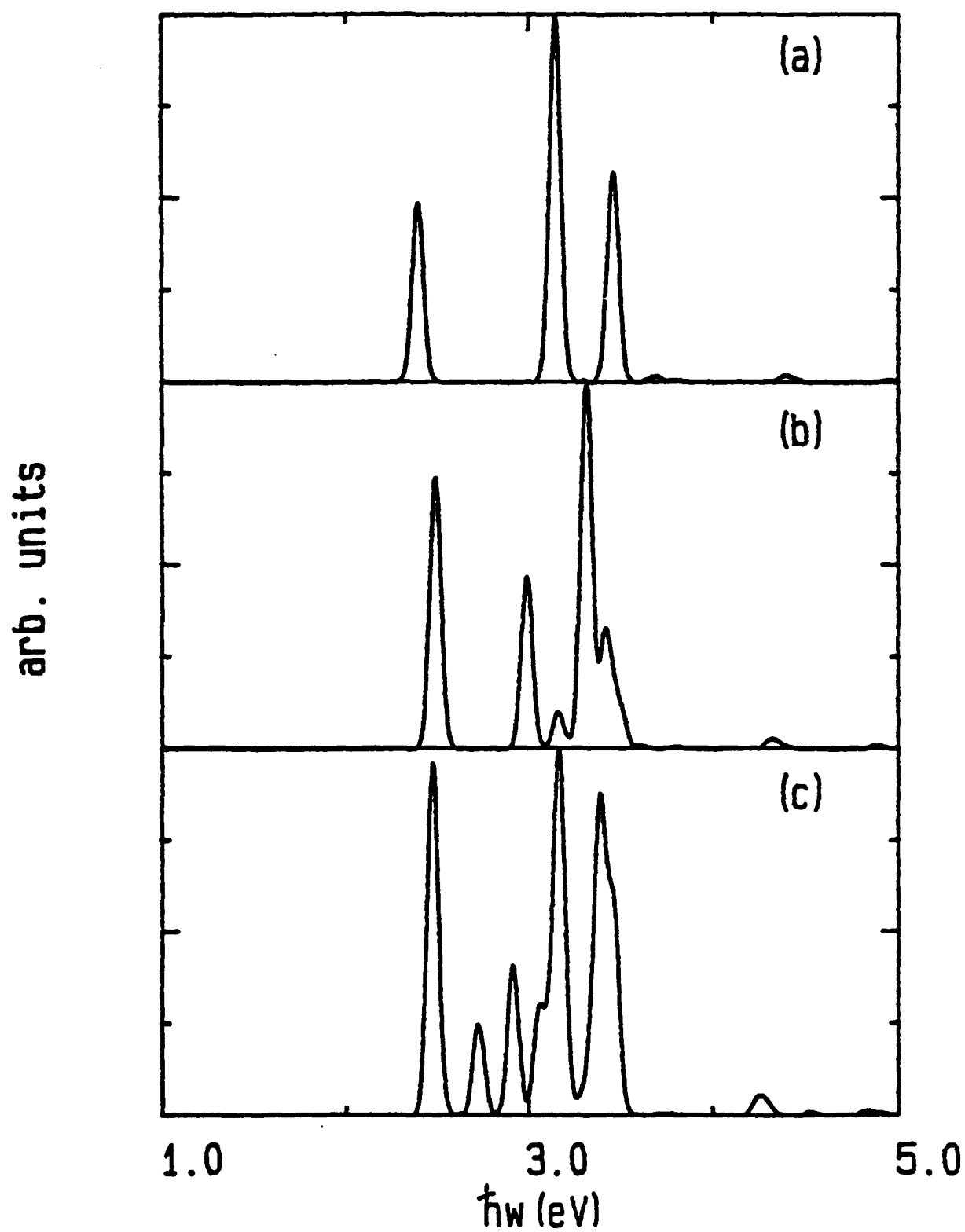


Fig. 11

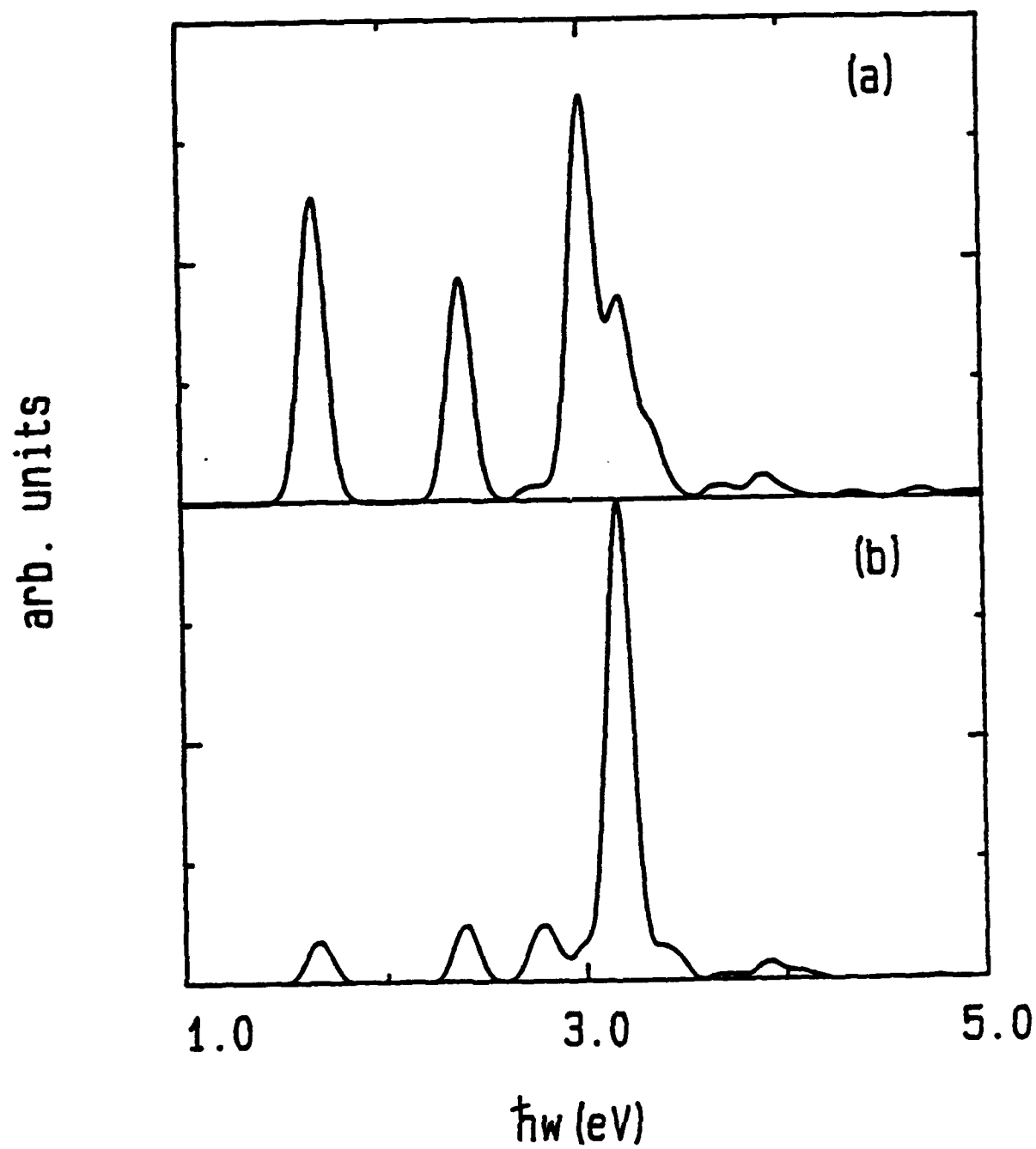
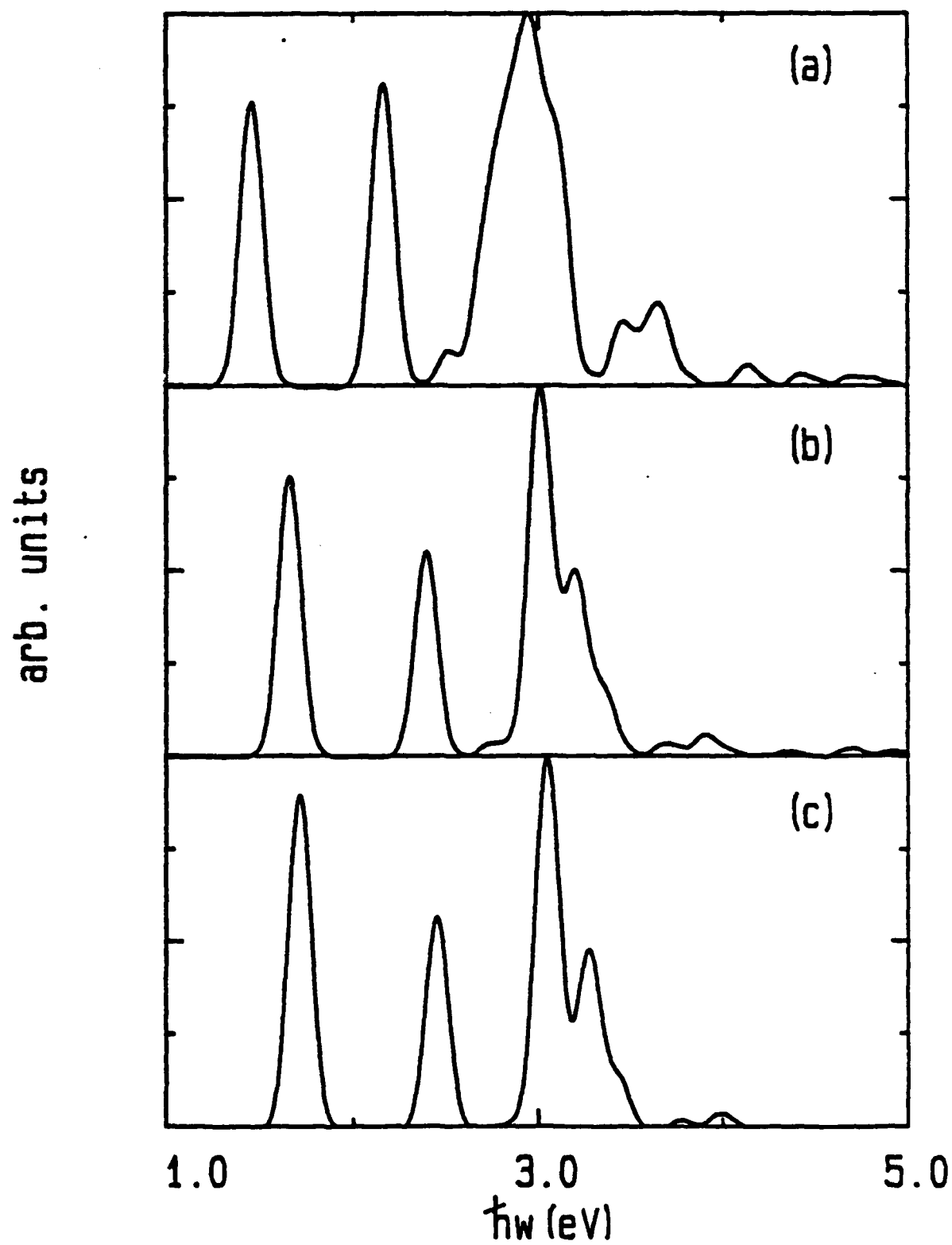


Fig. 12



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